Cycloaddition Reactions of Dicarbonyl(η^5-cyclopentadienyl)(η^1-indenyl)iron

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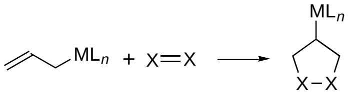
Summary: [3 + 2]-Cycloaddition reactions of the title compound with maleic anhydride and tetracyanoethylene form benzonorbornene derivatives. Dimethyl fumarate, dimethyl acetylenedicarboxylate, and diethyl azodicarboxylate do not react analogously. The reduced reactivity of indenyl−Fp compared to cyclopentadienyl−Fp supports the proposal that the latter reacts with electron-deficient alkenes by [4 + 2]-cycloaddition rather than [3 + 2]-cycloaddition.

The [3 + 2]-cycloaddition reaction of (η^1-allyl)metal compounds to form cyclopentanes (eq 1) is a reaction of both synthetic and mechanistic interest.[1] (η^1-Cyclopentadienyl)metal compounds are analogs of allylmetal compounds which are also capable of participating in cycloadditions;[2] however, for unsubstituted cyclopentadienylmetals, the product of [3 + 2]-cycloaddition across the 1,3-positions is identical to that expected from a Diels−Alder addition across the 2,5-positions (eq 2).[3] In principle, the two modes of cycloaddition could be distinguished by use of a substituted cyclopentadienylmetal compound, but in practice the low barrier to fluxional isomerization of the starting material makes this method impracticable. Thus, reaction of dicarbonyl(η^5-cyclopentadienyl)(η^1-methylcyclopentadienyl)iron [FpC_5H_4Me; Fp = $CpFe(CO_2)$−], which exists in solution as an equilibrating mixture of 2-methyl (major) and 1-methyl (minor) isomers, gave two isomeric cycloadducts upon reaction with dimethyl acetylenedicarboxylate (DMAD). Since the formation of each product could be rationalized in terms either of a [3 + 2]-addition to one isomer or a [4 + 2]-addition to the other,[4] no conclusion could be drawn concerning mechanism. Stereospecificity in the cycloadditions of maleonitrile and fumaronitrile to FpCp (in contrast to nonstereospecific [3 + 2]-additions of *E*- and *Z*-$F_3CC(CN){=}C(CN)CF_3$ and dimethyl maleate to $FpCH_2CH{=}CH_2$) has been taken to indicate a concerted [4 + 2] mechanism.[5] That the two processes are similar in energy requirements, however, is suggested by formation of [3 + 2]-adducts from the acyclic species $FpCH_2CH{=}CHCH{=}CRMe$ and TCNE or maleic anhydride when R = Me, in contrast to [4 + 2]-adducts when R = H.[6]



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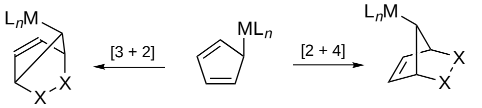
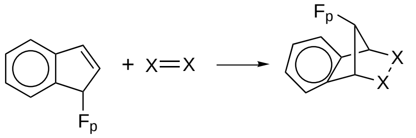


(2)

It occurred to us that further light could be shed on this mechanistic ambiguity by investigation of cycloaddition reactions of the (1-indenyl)metal compound, C_9H_7-Fp, **1**.[7] Lacking a diene unit, this substrate is incapable of participating in a Diels−Alder [4 + 2] reaction,[8] so that only [3 + 2]-cycloadditions should be found (eq 3). The products, 7-metalated benzonorbornenes, would be formal Diels−Alder adducts of the highly reactive 2*H*-indenes (isoindenes).[9] As such, they may have value as intermediates in the synthesis of polycyclic products.



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(3)

Results

The indenyliron compound, **1**, was readily prepared by reaction of indenyl-lithium and dicarbonylcyclopentadienyliron iodide (FpI) in THF at −78 °C. Use of low temperature consistently resulted in yields of 50 ± 10%, as compared to about 20% when the reaction was conducted at room temperature.[7] **1** reacted with maleic anhydride at room temperature in methylene chloride (or acetone), albeit slowly. Only one product was

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(9) Formation of analogous benzonorbornenes from 1-silyl- and 1-germylindenes has been interpreted in terms of trapping of an isoindene formed by 1,2-shift of the metal moiety: Ashe, A. J., III. *Tetrahedron Lett.* **1970**, 2105−9. Larrabee, R. B.; Dowden, B. F. *Tetrahedron Lett.* **1970**, 915−8. Luzikov, Yu. N; Sergeyev, N. M.; Ustynyuk, Yu. A. *J. Organomet. Chem.* **1974**, *65*, 303−10. Rigby, S. S.; Girard, L.; Bain, A. D.; McGlinchey, M. J. *Organometallics* **1995**, *14*, 3798−801. However, allylsilanes and -stannanes, which cannot plausibly isomerize in this manner, readily participate in [3 + 2]-cycloadditions: Knölker, H. J.; Jones, P. G.; Pannek, J. B. *Synlett* **1989**, *1*, 429−30. Herndon, J. W.; Wu, C.; Harp, J. J.; Kreutzer, K. A. *Synlett* **1991**, *2*, 1−10. Danheiser, R. L.; Takahashi, T.; Bertok, B.; Dixon, B. R. *Tetrahedron Lett.* **1993**, 3845−8. In the absence of kinetics studies to distinguish between the two possibilities, the simpler interpretation is that all of these reactions involve [3 + 2]-cycloadditions rather than prior isomerization of the metal group to C(2) of the indene.

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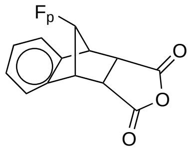
Table 1. Comparative Proton NMR Data for 2–4 and Related Adducts

adduct	C_6H_4 (δ)	$H_1 = H_4$ (δ)	$H_2 = H_3$ (δ)	H_7 (δ)	$J_{1,7}$ (Hz)	$J_{1,2}$ (Hz)	$J_{2,7}$ (Hz)	ref
2 (IndFp + MA)	7.20	3.69	3.75	2.83	<1	<1	<1	this work
3 (CpFp + MA)		3.34	3.54	2.59	0.8	nr	nr	3
$IndSnMe_3$ + MA	7.42	4.15	3.88	2.70	1.5	nr	nr	12
4 (IndFp + TCNE)	7.60, 7.42	4.55		3.23	<1			this work
$IndSiMe_3$ + TCNE	7.4	4.35		1.9	1.0			13
$IndGeMe_3$ + TCNE	7.52	4.85		2.33	1.17			14
Ind_2SiMe_2 + 2 TCNE	7.65, 7.46	4.93		2.35	1.05			15

Table 2. Comparative ^{13}C NMR Data for Adducts (δ)

adduct	$C_1 = C_4$	$C_2 = C_3$	$C_5 = C_6$	C_{benzo}	C_7	C_{Cp}	$C_{anhydride}$	C_{FeCO}	ref
2 (IndFp + MA)	58.2	50.7	144.4	127.8, 124.3	50.9	87.0	171.7	216.6	this work
3 (CpFp + MA)	56.8	48.2	135.5		50.8	85.6	171.0	216.5	3
Ind_2SiMe_2 + 2TCNE	60.5	51.3	140.7	130.5, 126.0	49.4				15

isolated, in 51% yield. Its IR and mass spectra were consistent with those expected for cycloadduct **2**. The similarity of its ^1H and ^{13}C NMR spectra (Tables 1 and 2) to those of the FpCp–maleic anhydride adduct, **3**, whose *anti*, *endo* structure has been confirmed by X-ray crystallography,[3] left no doubt that the structure of the adduct **2** was also *anti*, *endo*, as illustrated.



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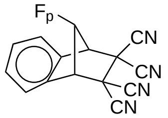

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Complete reaction of **1** with tetracyanoethylene (TCNE) required only a few minutes at room temperature. The NMR spectrum of the crude product showed only the adduct **4**, which was isolated in 93% yield. The NMR was uniquely consistent with structure **4**. In particular, the small $J_{1,7}$ in both **3** and **4** is most consistent with the 7-hydrogen being *syn* to the cyano or anhydride groups and the Fp group *anti*.[10] The structure **4** was also supported by IR, MS, and microanalytical data.

In contrast to TCNE and maleic anhydride, dimethyl fumarate (which reacted completely with FpCp in 4 h at room temp[4]) reacted sluggishly if at all with **1**. After 11 days, the NMR spectrum of the crude material still showed predominantly starting materials. (A GC-MS run revealed a small amount of a cyclopentadiene–dimethyl fumarate adduct.) Likewise, DMAD (which reacted with FpCp within 30 min at room temp[4]) failed to react within 1 day; heating **1** with DMAD in benzene resulted principally in decomposition of **1** with formation of 1,1′-biindenyl and Fp_2. Attempted reaction of **1** with diethyl azodicarboxylate resulted in formation of diethyl hydrazodicarboxylate and other products suggestive of free radical and redox processes, but there was no sign of a simple adduct.

Conclusion

The indenyliron compound, **1**, does give cycloaddition reactions formally analogous to those of its cyclopentadienyliron analog, FpCp. The maleic anhydride adduct, **2**, shows the same stereochemistry as the FpCp adduct, **3**. That stereochemistry is consistent with the formation of these adducts by a [3 + 2] mechanism, the only plausible mechanism for **1**. However, **1** reacted much more slowly with maleic anhydride than the cyclopentadienyl analog did (incomplete reaction after 6 days at room temperature for **1**, as compared to complete reaction within 30 min at 0 °C for FpCp[3]). The other dienophiles studied showed equally suppressed reactivity toward **1**, compared to FpCp. By far the simplest interpretation of the large rate differences is that FpCp reacts with electrophilic alkenes by a rapid Diels–Alder mechanism, whereas **1** can only avail itself of the slower [3 + 2] route. The reduced reactivity of dimethyl acetylenedicarboxylate (DMAD) compared to olefinic electrophiles, characteristic of the [3 + 2]-cycloaddition,[11] is manifested for **1** but not for FpCp.[3] The stereochemical results (previously cited[5]) also indicated a Diels–Alder [4 + 2] process in the FpCp cycloadditions. Interpretation of the results of the reaction of $CpFe(CO)_2(\eta^1\text{-}C_5H_4Me)$ with DMAD in terms of a Diels–Alder mechanism leads to the simple conclusion that the major isomer (2-methyl) of the starting material leads to the major product, and the minor isomer (1-methyl), similarly to the minor product.

The accord between all these results makes a persuasive case for the Diels–Alder path as the principal one for reactions of FpCp with electrophilic alkenes.

Experimental Section

Dicarbonyl(η^5-cyclopentadienyl)(η^1-indenyl)iron, 1.[7] A 100 mL round bottom flask equipped with magnetic stirrer, side arm with nitrogen inlet and rubber septum, and Nujol bubbler gas exit tube was flushed with nitrogen and then charged with 2.33 mL (2.32 g, 20.0 mmol) of indene, 50 mL of tetrahydrofuran (THF, distilled from sodium/benzophenone under nitrogen), and 8.4 mL of 2.5 M butyllithium in hexane (21 mmol of BuLi), all introduced by syringe while stirring. After 40 min at room temperature, during which time the solution became orange-colored, it was cooled in dry ice. Solid dicarbonylcyclopentadienyliron iodide (FpI, 6.134 g, 20.2 mmol) was added in one portion against a counterstream of nitrogen. Stirring was continued for 18 h, and then the solution was evaporated and the brown residue (12.5 g) chromatographed on silica. Elution with hexane and then 20% toluene/hexane yielded 2.76 g (47%) of product, which crystallized upon standing at 4 °C. Recrystallization from hexane at −80 °C gave a red-brown solid: mp 60–61.5 °C; lit.[7] mp 62–4 °C. IR: 2003, 1950 cm^{-1}.

Reaction of 1 with Maleic Anhydride. Maleic anhydride (0.200 g, 2.04 mmol) and **1** (0.500 g, 1.71 mmol) were stirred together in 25 mL of methylene chloride at room temperature under nitrogen. After 4 days, TLC and IR of the reaction mixture showed some **1** remaining, but the solvent was

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evaporated and the residue chromatographed on silica. Elution with 10−40% ethyl acetate/hexanes gave the adduct **2** (0.337 g, 51% crude yield). Attempts to recrystallize the adduct from several solvents and solvent mixtures gave an insoluble, light yellow powder, mp *ca.* 195 °C (dec), which tenaciously retained traces of solvents and could not be purified further. IR: 2000 and 1944 cm^{-1} (Fp); 1844 and 1774 cm^{-1} (anhydride). MS (*m/z*): 390, 362, and 334 (P − 0, 1, 2CO); 262 (P − 3CO − CO_2); 236 ($IndFeCp^+$); 121 ($FeCp^+$); 115 ($Ind^+ = C_9H_7^+$). ^1H NMR (300 MHz, $CDCl_3$): δ 7.20 (br s, 4H, benzo ring), 4.70 (s, 5H, Cp ring), 3.75 (br s, 2H, H_2 and H_3), 3.69 (br s, 2H, H_1 and H_4), 2.83 (br s, 1H, H_7). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 216.6 (Fe−CO), 171.7 (anhydride CO), 144.4 (C_5 and C_6), 127.8 and 124.3 (benzo ring), 58.2 (C_1 and C_4), 50.9 (C_7), and 50.7 (C_2 and C_3).

Reaction of 1 with Tetracyanoethylene. Freshly sublimed TCNE (0.225 g, 1.76 mmol) was added to a stirring solution of **1** (0.500 g, 1.71 mmol) in 30 mL of methylene chloride. The red-brown solution turned almost black. After 6 min, a drop of solution was removed and analyzed by TLC, using 25% ethyl acetate/hexane solvent. No remaining **1** could be detected. The solvent was evaporated, leaving 0.728 g of dark green solid whose ^1H NMR spectrum showed only peaks due to **4**. Washing with methylene chloride left 0.672 g (93%) of dark yellow solid, mp 125 °C (dec). ^1H NMR (300 MHz, $CDCl_3$): δ 7.60 and 7.42 (m, each 2H), AA′BB′ pattern of benzo ring; 5.09 (s, 5H), Cp; 4.55 (s, 2H), H_1 and H_4; 3.23 (s, 1H), H_7. The mass spectrum indicated cycloreversion, showing peaks for $IndFeCp^+$ (*m/z* 236), $CpFe(CO)_{2,1,0}{}^+$ (177, 149, 121), $TCNE^+$ (128), and Ind^+ (115). The IR spectrum (KBr pellet) consistently showed four carbonyl peaks, at 2020, 2011, 1968, and 1947 cm^{-1}, and a weak nitrile absorption at 2246 cm^{-1}. In acetone solution the carbonyl peaks appeared at 2014 and 1959 cm^{-1}. Anal. Calcd for $C_{22}H_{12}FeN_4O_2$: C, 62.88; H, 2.88; N, 13.33. Found: C, 62.50; H, 2.78; N 13.30.

Attempted Reaction of 1 with Dimethyl Fumarate. Dimethyl fumarate (0.261 g, 1.81 mmol) and **1** (0.500 g, 1.71 mmol) were stirred together in 30 mL of methylene chloride at room temperature under nitrogen. After 11 days, the solvent was evaporated even though the TLC showed mostly unconsumed starting materials. IR and NMR spectra of the residue showed substantial dimethyl fumarate. Silica chromatography, eluting with 20% ethyl acetate/hexanes, gave a fraction (0.251 g) which was predominantly recovered dimethyl fumarate. GC-MS analysis of this material showed one peak in addition to the recovered diester, which appeared to be the cyclopentadiene−dimethyl fumarate Diels−Alder adduct, dimethyl *trans*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (*m/z* 66, 113, 145, 91, 179). IR and NMR peaks in the fraction were consistent with formation of this product.[12]

Attempted Reaction of 1 with Dimethyl Acetylenedicarboxylate. DMAD (0.22 mL, 0.25 g, 1.74 mmol) and **1** (0.500 g, 1.71 mmol) were stirred together in 25 mL of methylene chloride at room temperature under nitrogen. After 1 day, the solution was evaporated. IR, NMR, and TLC of the residue showed only recovered starting materials, so it was taken up in 50 mL of benzene and refluxed under nitrogen. After 18 h, the TLC showed no **1** present. Chromatography on silica yielded 0.06 g (30%) of 1,1′-biindenyl as a 1:1 mixture of diastereomers, which eluted with 10% benzene/hexanes and was identified by TLC, IR, and NMR comparison with an authentic sample.[13] Elution with *ca.* 40% benzene/hexanes gave 0.07 g (28%) of recovered DMAD. The IR spectrum of the final fraction, eluted with ethyl acetate, indicated the presence of tetracarbonyldicyclopentadienyldiiron, Fp_2.

Attempted Reaction of 1 with Diethyl Azodicarboxylate. Diethyl azodicarboxylate (0.32 mL, 0.35 g, 2.04 mmol) and **1** (0.503 g, 1.72 mmol) were stirred together in 25 mL of methylene chloride at room temperature under nitrogen. After 18 h, several products were evident by TLC, so the solvent was evaporated. Chromatography on silica gel failed to yield pure products. GC-MS of a major fraction which eluted with methylene chloride revealed ferrocene, bi- and tricyclopentadienyl, and other, unidentified compounds. A later fraction which eluted with 70% ethyl acetate/methylene chloride showed major amounts of diethyl hydrazodicarboxylate (confirmed by GC-MS comparison with authentic sample) and an isomer (diethyl 1,1-hydrazinedicarboxylate?).

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